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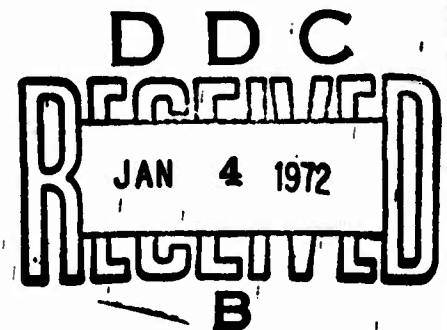
FOREIGN TECHNOLOGY DIVISION



INTERFACIAL ENERGY ON THE BOUNDARY BETWEEN A LIQUID METAL AND PYROLYTIC GRAPHITE

by

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A. V. Kharimonov



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| 13. ABSTRACT <p>→ An attempt was made to determine the interfacial energy on the boundary between a liquid metal (Ti and Zr) and pyrolytic graphite through the capillary action of the metal between graphite plates. The deviation of the reaction from the monomolecular case was determined. Orig. art. has: 3 figures, 3 equations.</p> | | | |

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METAL AND PYROLYTIC GRAPHITE

By: V. P. Yelyumin, V. I. Kosmikov, and A. V. Kharimonov

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U. S. BOARD ON GEOGRAPHIC NAMES TRANSLITERATION SYSTEM

| Block | Italic | Transliteration | Block | Italic | Transliteration |
|-------|------------|-----------------|-------|------------|-----------------|
| А а | <i>А а</i> | A, a | Р р | <i>Р р</i> | R, r |
| Б б | <i>Б б</i> | B, b | С с | <i>С с</i> | S, s |
| В в | <i>В в</i> | V, v | Т т | <i>Т т</i> | T, t |
| Г г | <i>Г г</i> | G, g | У у | <i>У у</i> | U, u |
| Д д | <i>Д д</i> | D, d | Ф ф | <i>Ф ф</i> | F, f |
| Е е | <i>Е е</i> | Ye, ye; E, e* | Х х | <i>Х х</i> | Kh, kh |
| Ж ж | <i>Ж ж</i> | Zh, zh | Ц ц | <i>Ц ц</i> | Ts, ts |
| З з | <i>З з</i> | Z, z | Ч ч | <i>Ч ч</i> | Ch, ch |
| И и | <i>И и</i> | I, i | Ш ш | <i>Ш ш</i> | Sh, sh |
| Я я | <i>Я я</i> | Y, y | Щ щ | <i>Щ щ</i> | Shch, shch |
| К к | <i>К к</i> | K, k | Ъ ъ | <i>Ъ ъ</i> | " |
| Л л | <i>Л л</i> | L, l | Ы ы | <i>Ы ы</i> | Y, y |
| М м | <i>М м</i> | M, m | Ь ь | <i>Ь ь</i> | ' |
| Н н | <i>Н н</i> | N, n | Э э | <i>Э э</i> | E, e |
| О о | <i>О о</i> | O, o | Ю ю | <i>Ю ю</i> | Yu, yu |
| П п | <i>П п</i> | P, p | Я я | <i>Я я</i> | Ya, ya |

* ye initially, after vowels, and after ъ, ь; e elsewhere.
 When written as ѣ in Russian, transliterate as yĕ or ĕ.
 The use of diacritical marks is preferred, but such marks
 may be omitted when expediency dictates.

INTERFACIAL ENERGY ON THE BOUNDARY
BETWEEN A LIQUID METAL AND PYRO-
LYTIC GRAPHITE

V. P. Yelyumin, V. I. Kosmikov and
A. V. Kharimonov

At present no methods exist for the direct experimental determination of the free interfacial energy on a liquid/solid body boundary.

In this work an effort is made to determine the interfacial tension on the boundary between a liquid metal and pyrolytic graphite. Titanium and zirconium were used as the liquid metals. Before the experiments the Obreymov and Gilman [spelling is not confirmed - translator] method was used to determine the free surface energy of the pyrolytic graphite; this turned out to be 1800 erg/cm^2 at room temperature. The procedure for determining the free interfacial energy involved using the rising of metal between two plane-parallel plates (Fig. 1). The dependence of the height of metal rise h on the distance between the plates, d , can be easily obtained from the Laplace equation:

$$h = \frac{2(\sigma_{s-l} - \sigma_{s-g})}{\rho g d}, \quad (1)$$

where σ_{s-g} — the surface tension of the solid body; σ_{s-l} — interfacial tension on the solid/liquid boundary; ρ — density of the liquid; g — gravity acceleration.

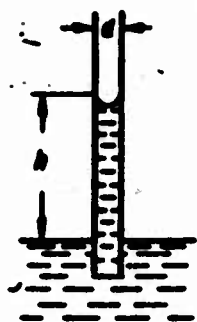


Fig. 1. Diagram of experiment.

After experimental measurements of the height of rise of metal between two parallel plates separated at a given distance d , it is possible to determine the difference $\sigma_{r-f} - \sigma_{r-m}$. If the free surface energy of the solid body is known, it is easy to determine the free interfacial energy on the solid/liquid boundary.

The metal was melted in a graphite crucible. Parallel plates of pyrolytic graphite were immersed in the molten metal and held for 1 h at a temperature exceeding the melting temperature of the metal by 50-100 degrees. The experiments were carried out in a TVV-4 furnace in a vacuum of 5×10^{-4} mm Hg. The height of rise of the metal was determined after the experiment.

The dependence of the height of metal rise on the distance between the plates was checked beforehand. From Fig. 2 it is clear that h and d are connected by an inversely proportional relationship. The nature of the change in the meniscus of the metal as a function of distance d is shown on Fig. 3. With an increase in the distance between the plates in the interval from 1 to 3 mm the bottom edge of the meniscus is lowered. This is apparently connected with the fact that initially the liquid metal "crawls" to the pyrolytic graphite plates and then draws up the remaining portion of the liquid. It is obvious that with an increase in the distance between the plates an ever greater mass of metal is attracted and the lower edge of the meniscus is dropped. Therefore in all cases the distance from the level of metal in the crucible to the maximum point of metal rise was taken as the height of rise of the metal.

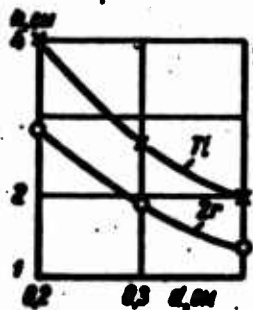


Fig. 2.

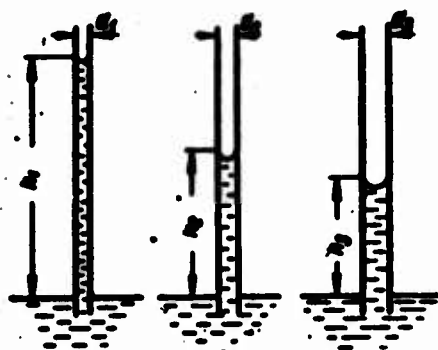


Fig. 3.

Fig. 2. Height of rise of the metal, h , as a function of the distance d between the plates.

Fig. 3. Shape of the meniscus as a function of the distance d between the plates.

The obtained data have the following values:

| M | t_{exp} $^{\circ}C$ | ρ when t_{exp} g/cm^3 | d, cm | h, cm | $\sigma_{T-r} - \sigma_{T-m}$ erg/cm^2 | σ_{T-r} for pyro- lytic graphite t_{exp} erg/cm^2 | σ_{T-m} erg/cm^2 | $\sigma_{T-m, av.}$ erg/cm^2 |
|-----|--------------------------|---|---|---|--|---|---|-----------------------------------|
| Ti | 1600 | 4.11 [1] | $\begin{Bmatrix} 0.2 \\ 0.3 \\ 0.4 \end{Bmatrix}$ | $\begin{Bmatrix} 4.0 \\ 2.6 \\ 2.0 \end{Bmatrix}$ | $\begin{Bmatrix} 1610 \\ 1580 \\ 1620 \end{Bmatrix}$ | 1640 | $\begin{Bmatrix} +30 \\ +60 \\ +30 \end{Bmatrix}$ | +40 |
| Zr | 1800 | 6.1 [1] | $\begin{Bmatrix} 0.2 \\ 0.3 \\ 0.4 \end{Bmatrix}$ | $\begin{Bmatrix} 2.8 \\ 1.9 \\ 1.4 \end{Bmatrix}$ | $\begin{Bmatrix} 1680 \\ 1710 \\ 1650 \end{Bmatrix}$ | 1620 | $\begin{Bmatrix} -80 \\ -90 \\ -80 \end{Bmatrix}$ | -70 |

The values of density of the liquid metals were taken at the melting temperatures of the corresponding metals [1, 2]. As was noted above, the free surface energy of pyrolytic graphite was determined at room temperature, while the experiments were carried out at temperatures of 1600 and 1800°C. It is necessary to introduce the appropriate correction for reduction of free surface energy of the pyrolytic graphite with the increase in temperature. At present the temperature coefficient of surface energy of pyrolytic graphite is unknown, but it can be taken as equal to 0.1 erg/cm^2 , as for the majority of solids. The values of surface energy of pyrolytic graphite at the experimental temperatures are given above, with account taken of the temperature coefficient.

After substituting all values into equation (1) we obtain the value of the interfacial energy for Ti and Zr. It turned out that the interfacial tension of zirconium on a boundary with pyrolytic graphite comprises -70 erg/cm^2 , with the value for titanium being $+40 \text{ erg/cm}^2$; this corresponds to common presentations on interfacial energy for intensively interacting systems [3].

In work [4] the authors carried out a quantitative examination of the influence of chemical reaction on interfacial energy on a solid/liquid boundary on the basis of equilibrium thermodynamics. They found that

$$\sigma_{z-l} = \sigma_{z-l} - \sigma_{z-l} + \frac{\Delta F_p}{s}, \quad (2)$$

If the reaction proceeds in a single layer (s — area of a mole of the liquid; ΔF_p — free energy of the chemical reaction).

In the case when there is reaction in systems of refractory metals from group IV and pyrolytic graphite, calculations according to equation (2) are scarcely applicable, since the speed of diffusion of carbon into the liquid metal is great and the action does not occur in a single layer. However, it is of interest to evaluate the deviation of the reaction from the single layer for the case of reactions in such systems. Equation (2) can be written as follows:

$$\sigma_{z-l} = \sigma_{z-l} - \sigma_{z-l} + \frac{\Delta F_p \cdot 4.18 \cdot 10^7}{s}. \quad (3)$$

Here $s = K \left(\frac{M}{\rho} \right)^{\frac{2}{3}} N^{\frac{1}{3}}$ is the area of a single mole stretched out into a single layer (K — a coefficient approximately equal to 1; M — molecular weight; ρ — density; N — Avogadro number; n — number of single layers); $4.18 \cdot 10^7$ — coefficient for conversion of cal into erg.

The following results were obtained:

| Mn | | AP _p | |
|----|----------------------|-----------------------|----|
| | | cal/mole | n |
| | | when t _{exp} | |
| Ti | 43.7·10 ⁷ | -40000 [5] | 19 |
| Zr | 51.5·10 ⁷ | -50000 [5] | 16 |

It was found that in actuality the reaction does not occur in a single layer, but over a thickness of about 19 monolayers for Ti and 16 layers for Zr. The greater number of single layers in the case of titanium is explained by the large coefficient of carbon diffusion into titanium as compared with diffusion of zirconium [5].

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